

Universality of the Scaling Law for Ferroic Domains

G. Catalan^{1,*}, J. F. Scott¹, A. Schilling², and J. M. Gregg²

¹ *Department of Earth Sciences, University of Cambridge,
Downing Street, Cambridge CB2 3EQ, United Kingdom and*

² *International Research Center for Experimental Physics (IRCEP),
Queen's University of Belfast, Belfast BT7 1NN, United Kingdom*

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We show how the periodicity of 180° domains as a function of crystal thickness scales with the thickness of the domain walls both for ferroelectric and for ferromagnetic materials. We derive an analytical expression for the universal scaling factor and use this to calculate domain wall thickness and gradient coefficients (exchange constants) in some ferroic materials. We then use these to discuss some of the wider implications for the physics of ferroelectric nano-devices and periodically poled photonic crystals.

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The generic term "ferroic" designates crystalline materials that are ordered either ferroelectrically, ferromagnetically or ferroelastically (including also antiferroic configurations). Ferroic materials usually display domains, that is, regions that are either ordered along different polar directions or along the same direction but with opposite polarity (180° domains). Kittel showed some 60 years ago that the width of 180° magnetic domains (w) is correlated to the thickness of a crystal in a very well defined manner: the square of the domain width (w) is directly proportional to the thickness of the crystal (d) [1]. Kittel's law was latter extended by Mitsui and Furuichi (1953) for ferroelectric materials [2], and by Roytburd (1972) for epitaxially clamped ferroelastic ones [3].

Recently, Schilling et al. [4] have shown that the constant of proportionality between w^2 and d is a defining characteristic of the type of ferroic transition being considered, with ferromagnets having generally bigger domains than ferroelectrics for crystals of the same thickness. These experimental results were rationalised by Scott [5], who observed that the differences between ferroelectric and ferromagnetic domain periodicity essentially disappeared once the domain wall thickness was incorporated as a scaling factor. Mathematically this was expressed as $\frac{w^2}{Td} = M$, where T is the thickness of the domain wall and d is the crystal thickness; since domain walls tend to be narrow (few unit cells) for for all ferroelectrics, and broader for ferromagnets (tens of nanometers), the dimensionless factor M ends up being pretty much the same for both. This is nicely illustrated in Figure 1: the different characteristics for w^2 as a function of crystal thickness of ferroelectrics and ferromagnets fall into the same parent curve once the square of the domain width is scaled by the domain wall thickness T .

In this Letter we discuss the nature of the dimensionless constant M , and derive a simple analytical expression

for it. We then use the result to calculate the thickness of domain walls in several ferroic materials, and discuss some of the wider implications for practical applications.

We begin by writing the Landau thermodynamic potential describing a second-order phase transition in a ferroic. For simplicity's sake, we shall focus on the case of 180° walls in a uniaxial ferroic, so a single order parameter will suffice. We call this order parameter Q , and it can be either the polarization or the magnetization, depending on the type of ferroic being considered. Across a domain wall there is a change of the sign of the order parameter. That means that there is necessarily a gradient, whose associated energy must be incorporated into the thermodynamic potential. Assuming that Q points along the z direction and that the domain wall is perpendicular to the x axis, the thermodynamic potential is

$$\Delta G = \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{k}{2}\left(\frac{\partial Q}{\partial x}\right)^2 \quad (1)$$

For a mono-domain state, and also for the center of the domains, we can neglect the gradient term, and minimization then leads to the familiar result for the order parameter in the ferroic state:

$$Q_0^2 = -\frac{a}{b} \quad (2)$$

The second derivative of the free energy with respect to the order parameter is the stiffness. In the ferroic state, the result is $\chi_c^{-1} = -2a$ or, relating this to the order parameter,

$$\chi_c^{-1} = 2bQ_0^2 \quad (3)$$

Here the term "stiffness" has different meanings depending on the ferroic context, being inverse permittivity for ferroelectrics and inverse susceptibility for magnets.

The energy density of the domain wall is calculated by minimizing the energy difference between a mono-domain state and a state with one domain wall. That is, one has

*Electronic address: gcat05@esc.cam.ac.uk

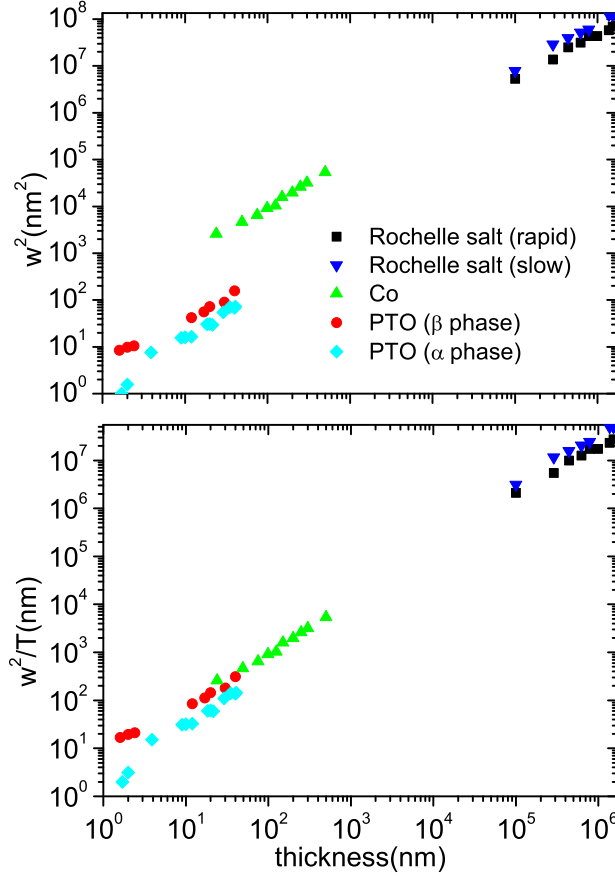


FIG. 1: (Color online) Above: Square of the 180° domain width as a function of crystal thickness for some ferroics (data extracted from refs. [2, 17, 25]). Below: When the square of the domain width is divided by the wall thickness, all data-points fall essentially on the same parent curve. The domain wall size used for the scaling has been extracted from refs. [2, 7, 21]

to minimize the following [2, 6]:

$$\sigma = \int_{-\infty}^{+\infty} \left(\frac{a}{2} (Q^2 - Q_0^2) + \frac{b}{4} (Q^4 - Q_0^4) + \frac{k}{2} \left(\frac{\partial Q}{\partial x} \right)^2 \right) dx \quad (4)$$

Where Q_0 is given by eq. (2). Minimization of σ with the boundary condition $Q(x=\pm\infty) = Q_0$ leads to the solution of the profile of the order parameter across the domain wall $Q(x) = Q_0 \tanh(x/\delta)$, where the characteristic thickness is

$$\delta = \frac{1}{Q_0} \sqrt{\frac{2k}{b}} = \sqrt{-\frac{2k}{a}} \quad (5)$$

and the energy density of the domain wall is

$$\sigma = \frac{4}{3} Q_0^3 \sqrt{2kb} = \frac{4}{3} Q_0^2 \sqrt{-2ka} \quad (6)$$

Several important simplifications have been made in the above treatment. First, in constraining the order

parameter to just one dimension we have implicitly discarded the possibility of Bloch walls and Neel walls. This is in principle wrong for magnetic materials (though not for ferroelectrics). However, the analysis of such walls in magnetic materials actually arrives at the same solutions [7]. Second, in limiting our Landau expansion to the Q^4 order, we are limiting ourselves to second order transitions, which is not the case for several important ferroelectrics such as PbTiO_3 and BaTiO_3 , although in thin films of these two materials epitaxial clamping (regardless of strain) changes the transition from first to second order [8, 9]. For the exact solution of the first order domain wall the reader is advised to look at ref. [10]. And third, we have neglected the elastic coupling to the lattice distortions (strain terms), which is particularly important in ferroelectrics as they generally are also ferroelastic. However, the effect of strain can be incorporated by a renormalization of the coefficients in the Landau expansion [6, 8, 9, 11], so our treatment is still be valid once the renormalized coefficients are used.

Regarding the physical interpretation of eq.5, k represents an "exchange" constant, as its energy contribution is proportional to the mismatch of spins/dipoles with respect to their neighbors (gradient term) whereas a and b represent the "anisotropy" contributions, as they indicate the strength of the alignment of the order parameter with respect to the crystallographic axes. Quite naturally, it follows that if the anisotropy terms are big, the domain walls will tend to be narrow so as to minimize the number of misaligned spins/dipoles, whereas if the exchange k is big the domain walls will tend to be wide so that the gradient is as small as possible. In magnets, the exchange interaction wins, whereas in ferroelectrics the opposite is true, hence the difference in domain wall thickness generally observed between the two types of ferroic [4, 6].

The exchange constant k is well characterized for most magnetic materials, but that is not the case for ferroelectrics [12], a problem which has so far complicated analysis based on eqs. 9 and 6. It is therefore interesting to write the energy density as a function of domain wall thickness, which removes the dependence on k :

$$\sigma = \frac{4}{3} Q_0^4 b \delta = -\frac{4}{3} Q_0^2 a \delta \quad (7)$$

This expression will be used later.

We turn now to the relation between domain periodicity and thickness in a crystal slab cut perpendicular to the polar direction. The uncompensated dipoles/spins at the surface generate a large electrostatic/magnetostatic energy, which is reduced by creating domains of opposite polarity. The depolarization/demagnetization energy of the two crystal surfaces as a function of domain width is:

$$F_{\text{surface}} = \frac{7\zeta(3)Q_0^2}{\pi^3} \sqrt{\chi_a \chi_c} w \quad (8)$$

Where $\zeta(3)$ is Riemann's zeta function $\zeta(3) \simeq 1.202$ [13]. Although the physical forces involved (electrostatic, mag-

netostatic) are different, the Maxwell equations for the energy are analogous, and thus the resulting expression for the surface energy ends up being much the same [1, 2, 7, 15, 16]; the difference between the two ferroics is thus not contained in the shape of the equation, but only in the magnitudes involved: the order parameter Q (polarization/magnetization) and the permittivity/susceptibility χ .

The reduction in surface energy achieved by introducing domains is of course partly offset by the energy cost of the domain walls, which is proportional to σ , to the wall size (itself proportional to the crystal thickness d) and to the number density of domain walls (inversely proportional to the domain width w). Hence, $F_{wall} = \sigma d/w$. Adding the two energy components and minimizing with respect to the domain width w leads to the standard result

$$w^2 = \frac{\pi^3 \sigma \sqrt{\chi_a \chi_c}}{7\zeta(3)Q_0^2} d \quad (9)$$

If we now substitute the order parameter Q_0 and the energy density σ by their respective expressions from eqs. 2 and 7, the final expression for the dimensionless factor is:

$$M \equiv \frac{w^2}{d\delta} = \frac{2}{3} \frac{\pi^3}{7\zeta(3)} \sqrt{\frac{\chi_a}{\chi_c}} \simeq 2.455 \sqrt{\frac{\chi_a}{\chi_c}} \quad (10)$$

The experimental observation that M is generally a number in the range 1-10 for any ferroic is thus explained: the result is always a numerical constant ($\simeq 2.455$) modified by the square root of the susceptibility anisotropy. The appeal of this expression is not just in its simplicity and generality, but also in that it can actually be exploited for practical purposes.

It has been a long standing and challenging problem to establish the thickness of domain walls in ferroics, and very specially in ferroelectrics, as the latter tend to be very thin and hard to measure experimentally [18, 19, 20]. On the other hand, theoretical approaches based on phenomenological models suffered from the fact that the coefficient k of the gradient term is hard to characterize experimentally. Equation 10 dispenses the need to know such a coefficient. Measuring domain width and crystal thickness and knowing the dielectric constants of a material should be enough to estimate the domain wall width. So does it work?

In figure 1 we have shown the square of the domain width as a function of crystal thickness for 180° domains in ferroelectric $PbTiO_3$ and Rochelle Salt, and ferromagnetic Co. All of them can be analyzed with the present treatment, although in the case of the PTO films a correction due to the effect of the substrate must be taken into account [15, 17]. The measured slope, the permittivities and the calculated thickness of the 180° domain walls are shown in table 1, next to previous values extracted from the literature.

material	$\delta M(\text{nm})$	ϵ_x	ϵ_z	$\delta(\text{\AA})$	$\delta_{previous}(\text{\AA})$	$k(\text{m}^3/\text{F})$
Rochelle Salt	21	445	9.8	13	12-22[2]	9×10^{-11}
$PbTiO_3$	3.5	124	66	2.45	$\simeq 2[21]$	2.8×10^{-11} [32]

TABLE I: Experimental slope of w^2 vs d for 180° domains in two ferroelectrics (slope= δM), calculated thickness of the domain walls and calculated value of the exchange constant k . The Landau coefficients used in the calculations have been extracted from refs. [2] and [8]. The domain wall thickness is compared with previous published estimates

Our predicted value for δ of the Rochelle Salt is 13\AA (and thus the wall thickness is $T = 2\delta = 26\text{\AA}$), compatible with the results of Mitsui and Furuichi ($T=24-47\text{\AA}$) [2], and Zhirnov ($\delta=12-220\text{\AA}$) [6]. As for the predicted value for the domain walls of PTO, once the effect of the STO substrate has been taken into account [15, 17] we obtain that $\delta=2.45\text{\AA}$ or $T=4.9\text{\AA}$, in excellent agreement with the first principle calculations of Meyer and Vanderbilt [21]. The combination of our model with experimental data thus agrees with previous estimates, and support the view that ferroelectric 180° domain walls are atomically sharp [22, 23].

The above equations apply to magnetic materials too. Fitting the data of Co to our model, the calculated domain wall thickness is 20nm , which is somewhat thicker than previous theoretical estimates that yield a value of 5-10nm, but thinner than the experimentally determined values of 46nm [24]. All in all, the results suggest that the method is quite robust for the analysis of different ferroics.

Moreover, once the domain wall thickness has been determined, one can go back to eq. 5 and determine the value of the exchange constant (k) for the material, which is also a long standing challenge in ferroelectrics [12]. It is worth emphasizing here that this constant is of great importance in determining the performance of ferroelectric thin films and nanostructures [5, 26], where the gradient term associated with the surface depolarization has a strong effect on the functional properties [27, 28, 29, 30, 31]. Our calculated values of k for $PbTiO_3$ and Rochelle salt are included in table 1.

Parenthetically, we note also that regular domains in ferroelectric crystals have important applications in photonics, where they are used for frequency conversion through quasi phase matching [33]. Presently, the regularly spaced stripe domains are achieved through periodic poling, which has limitations due to the large coercive field -and some times finite conductivity- of some of the most important photonic crystals, such as $LiNbO_3$ and $KTiOPO_4$ (KTP). Importantly also, artificially fabricated domain structures are generally not in thermodynamic equilibrium, and switchback can occur [34]. In theory it should be possible to achieve self-patterned and stable regular domains in ferroelectric photonic crystals by cutting them at the right thickness and preventing

charge screening upon cooling through the phase transition, although in practice periodic poling is always likely to be required (e.g. to maximize registration). As a practical example of reverse engineering, the measured value of the domain wall thickness for KTP is 3Å[19], while the longitudinal and transverse relative permittivities are 15 and 11 respectively [35]; accordingly, a periodic domain structure with a domain width of e.g. 5 microns would be most stable for a crystal $\simeq 3\text{cm}$ thick or, conversely, a 0.5mm crystal of KTP can have domains as small as $0.7\mu\text{m}$. This suggests that the known difficulty in stabilizing narrow domains in thick crystals is not due to intrinsic factors; indeed, experiments that make use of the depolarizing field have achieved self-patterned sub-micron domains in LiNbO_3 [36].

In sum, the universal scaling law for ferroic domains

provides a versatile and powerful tool for analyzing the physical properties of ferroic materials in general, and ferroelectrics in particular. Our own analysis of existing data suggests that the thickness of 180° domain walls in ferroelectrics is extremely narrow (of the order of one unit cell), and that regular patterns of sub-micron domains can be achieved in photonic crystals. More studies of domain periodicity as a function of crystal thickness should be carried out to establish domain wall thickness and exchange parameters for other relevant ferroelectrics such as LiNbO_3 and BaTiO_3 .

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- [1] C. Kittel, Phys. Rev. **70**, 965 (1946)
- [2] T. Mitsui, J. Furuichi, Phys. Rev. **90**, 193 (1953).
- [3] A. Roytburd, Phys. Status Solidi A **37**, 329 (1976).
- [4] A. Schilling, T. B. Adams, R. M. Bowman, J. M. Gregg, G. Catalan, J. F. Scott, PRB **74**, 024115 (2006).
- [5] J.F. Scott, J. Phys. Cond. Mat. **18**, R361 (2006).
- [6] V. A. Zhirnov, Sov. Phys. JETP **35**, 822 (1959).
- [7] A. Hubert, R. Schäfer, *Magnetic Domains* (Springer-Verlag, Berlin 1998).
- [8] N. A. Pertsev, A. G. Zembilgotov, A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
- [9] G. Catalan, L.J. Sinnamon, J. M. Gregg, J. Phys. Cond. Mat. **16**, 2253 (2004).
- [10] W. Cao, L.E. Cross, Phys. Rev. B **44**, 5 (1991).
- [11] M. E. Lines, A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, Oxford 1977).
- [12] W. Cao, J. Phys. Soc. Jpn. **63**, 1156 (1994).
- [13] Calculating the energy involves integrating the Fourier series of a square-wave of period $2w$ and amplitude proportional to Q^2 ; the zeta function appears as follows:

$$\sum_{n=0}^{\infty} \frac{1}{(2n+1)^3} = (1 - \frac{1}{2^3}) \sum_{n=1}^{\infty} \frac{1}{(n)^3} = \frac{7}{8}\zeta(3)$$
- [14] T. Ozaki and J. Ohgami, J.Phys. Cond. Mat. **7**, 1711 (1995)
- [15] J. L. Bjorkstam, R. E. Oettel, Phys. Rev. **159**, 427 (1967).
- [16] A. Kopal, T. Bahnik, and J. Fousek, Ferroelectrics **202**, 267 (1997).
- [17] S. K. Streiffer, J. A. Eastman, D. D. Fong, C. Thompson, A. Munkholm, M. V. RamanaMurthy, O. Auciello, G. R. Bai, and G. B. Stephenson, Phys. Rev. Lett. **89**, 67601 (2002).
- [18] N. Floquet, C-M- Valot, M-T- Mesnier, J-C- Niepce, L. Norrmand, A. Thorel and R. Kilaas, J. Phys III **7**, 1105 (1997)
- [19] P Pernot-Rejmankova, P A Thomas, P Cloetens, T Lyford and J Baruchel, J. Phys.: Cond. Mat. **15**,1613 (2003).
- [20] D. Shilo, G. Ravichandran, K. Bhattacharya, Nature Materials **3**, 453 (2004).
- [21] B. Meyer and D. Vanderbilt, Phys. Rev. B **65**, 104111 (2002)
- [22] W. Kinase, H. Takahashi, J. Phys. Soc. Jpn. **12**, 464 (1957).
- [23] W. N. Lawless Phys. Rev. **175**, 619 (1968)
- [24] D. M. Donnet, K. M Krishnan and Y. Yajima, J. Phys. D: Appl. Phys. **28** 1942 (1995).
- [25] M. Hehn, S. Padovani, K. Ounadjela, and J. P. Bucher, Phys. Rev. B **54**, 3428 (1996).
- [26] M. Dawber, K. M. Rabe, J. F. Scott, Rev. Mod. Phys. **77**, 1072 (2005).
- [27] K. Binder, Ferroelectrics **35**, 99 (1981)
- [28] O.J. Vendik and S. P. Zubko, J. Appl. Phys. **88**, 5343 (2002)
- [29] A.G. Zembilgotov, N.A. Pertsev, H. Kohlstedt and R. Waser J. Appl. Phys. **91**, 2247 (2003)
- [30] M. D. Glinchuk and A. N. Morozovska, J. Phys.: Condens. Matter **16**, 3517 (2004).
- [31] A.M. Bratkovsky, A.P. Levanyuk, arXiv:cond-mat/0608283 (2006)
- [32] The coefficient k of PTO was calculated using the formula for first order phase transitions [10].
- [33] J.A. Armstrong, N. Bloembergen, J. Ducuing and P.S. Pershan Phys. Rev. **127**, 1918 (1962)
- [34] Robert G. Batchko, Vladimir Y. Shur, Martin M. Fejer, and Robert L. Byer, Appl. Phys. Lett. **75**, 1673 (1999).
- [35] J. D Bierlein, C. W. Arwiler, Appl. Phys. Lett. **49**, 917 (1996)
- [36] V. Ya. Shur, E. L. Rumyantsev, E. V. Nikolaeva, E. I. Shishkin, D. V. Fursov, R. G. Batchko, L. A. Eyres, M. M. Fejer, and R. L. Byer, Appl. Phys. Lett. **76**, 143 (2000).